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Thermal and FTIR Characterization of Poly (4-vinylpyridine) Crosslinked with Metal Salts

by Nicole E. Zander, Joshua A. Orlicki, and Adam M. Rawlett

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Nicole E. Zander, Joshua A. Orlicki, and Adam M. Rawlett
Weapons and Materials Research Directorate, ARL

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14. ABSTRACT

We investigated the physical properties and degree of crosslinking of poly (4-vinylpyridine) (P4VP) blended with transition metal salts using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The glass transition temperature (T_g) of the blends increased significantly upon addition of zinc (Zn) and copper (II) (Cu) salts. T_g enhancement was found to be highly dependent upon the type and loading of the metal salt. A maximum increase of 70 °C was observed at 0.25 molar equivalents of Zn cation. Ash content from TGA was highest for the 0.25 zinc salt loading, indicating that the maximum amount of metal ion was incorporated into the polymer at this concentration. Fourier transform infrared spectroscopy (FTIR) provided confirmation that transition metal coordination between the Zn cation and the pyridine nitrogens occured, and allowed for the quantification of pyridine binding.

15. SUBJECT TERMS

P4VP, Tg, FTIR, DSC, TGA, coordination chemistry

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1. Background

The intermolecular association between components in blends or composite interfaces plays a critical role in governing the physical properties of the system (*1*). The influence of hydrogen bonding in molecular dynamics at different length scales is well known. Intermolecular bonding can suppress localized β motions of the polymer chains at temperatures below the glass transition temperature (T_g) due to the formation of transient crosslinks between polymer chains. The mechanical properties, as well as aging of the polymer, are known to be related to these localized motions in the glassy state (*1*). Like hydrogen bonding, the addition of inorganic salts is a useful means to improve both the thermal and mechanical stability of a polymer system (*1–6*). Transition metal salts behave differently than low molecular weight plasticizers, in that they increase rather than decrease the T_g of the polymer by forming rigid coordination complexes. The degree of suppression of localized motion depends strongly on the strength of the interactions between the polymer backbone or pendant groups and the metal salt (*6*).

Poly-4-vinylpyridine (P4VP) is a polymer of interest due to its high electrical conductivity, though it suffers from low thermal and mechanical stability (*2, 5*). Overlap of the frontier molecular orbitals of the metal atoms with the neutral basic pyridine ligands in the polymer allows for network formation and enhanced interchain electron transfer (*1*). Previous research has demonstrated significant improvement in electrical conductivity of P4VP and poly-2-vinylpyridine (P2VP) with the addition of copper salts (*2, 5*).

Most research in this area of polymer blends has focused on using differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) data to qualitatively assess the degree of crosslinking. In this work, a quantitative correlation between the degree of crosslinking, and the amount of zinc salt added using thermal decomposition data and peak area integrations of FTIR spectra, is presented. In addition to zinc salts, the effect of non-covalent crosslinks with other transition, alkali, and alkaline earth metals on the physical properties of P4VP was investigated.

2. Materials and Methods

2.1 Materials

P4VP (Mw = 50 kDa), zinc chloride ($ZnCl_2$), copper (II) chloride ($CuCl_2$), magnesium chloride ($MgCl_2$), sodium chloride (NaCl), and potassium chloride (KCl) were obtained from Sigma Aldrich and used as received.

2.2 Methods

P4VP and metal salts at molar equivalent ratios of 1:1 to 1:100 were dissolved separately in ethanol at concentrations of approximately 10 wt % and 5 wt %, respectively. The metal ion solution was then added quickly to the stirring polymer solution, and the resulting mixture was stirred RT for 30 min. Mixtures with high loadings of metal ions, typically 1:1 to 1:10, formed insoluble complexes that were isolated by vacuum filtration, washed several times with ethanol, and dried in a vacuum oven (60 ºC, 24 hr). Semi-soluble and soluble mixtures were isolated by rotary evaporation, washed with water, centrifuged, and dried.

We prepared fully protonated P4VP (Mw = 50,000) by dissolving the polymer in methylene chloride and adding 20 μL of a 4M HCl solution. The mixture was stirred RT for 30 min, isolated by rotary evaporation, and dried in a vacuum oven.

FITR samples were prepared by grinding 10 mg of sample with 100 mg of potassium bromide and pressing into a transparent pellet.

2.3 Instrumental Analysis

Infrared spectra were collected using a FTIR spectrometer (Thermo Nicolet Nexus 870 ESP), using 64 scans and 2 cm^{-1} resolution. The thermal stability was characterized on a TA Instrument Thermogravimetric Analyzer (TGA Q 5000) under nitrogen flow. All samples were heated at 10 ºC/min to 700 ºC. Thermal properties were measured on a TA Instruments DSC with a heat/cool/heat program. All samples were heated at 10 ºC/min to 250 ºC, cooled 5 ºC/min to –20 ºC, and then heated again at 10 ºC/min to 250 ºC. The glass transition temperature was taken as the point of inflection in the glass transition region. DSC and TGA data were processed using Universal Analysis software. The T_g was automatically calculated by defining the limits of the glass transition region. The derivative weight (DTGA) was used for all TGA charts.

FTIR data was imported into CasaXPS software for peak integration and processing (*8*).

3. Results and Discussion

The physical properties of P4VP changed immediately with the addition of metal salts. For high loadings of metal salts (0.11 to 1 molar equivalents of zinc (Zn^{2+}) per P4VP nitrogen), a solid precipitate formed within seconds of addition. Lower loading levels produced either a gelatinous consistency or a soluble mixture. Molar equivalents as low as 0.01 still enhanced the physical properties of the polymer. Figure 1 displays glass transition data for the addition of Zn^{2+} to P4VP at molar equivalence ratios from 1:1 down to 1:100, respectively, as determined by DSC. As is shown, the addition of 0.01 (1:100) molar equivalents Zn^{2+} increases the T_g of neat P4VP from approximately 147 °C to 153 °C. The T_g continues to increase at higher loadings of Zn^{2+}

until it reaches a maximum at a 1:4 molar equivalent ratio (220 °C), which corresponds to a 70 °C enhancement over neat P4VP. Successively higher loading showed a suppression of the T_g, although it was still enhanced over the neat material. Thus, addition of the salt restricts the mobility of the polymer chains by forming physical crosslinks, which leads to an increase in the T_g up to the maximum observed at 1 Zn^{2+} for every four pyridine rings (tetrahedral coordination). The T_g drops off at higher loadings of Zn^{2+}, a condition frequently observed for polyelectrolytes (7). The strength of the polymer/salt and salt cation/anion interaction strongly governs polymer chain rigidity and intersegmental distances. Kim et al. found that for silver acetate/poly (2-ethyl-2-oxazoline) systems, the highest T_g was observed for a 1:3 molar equivalence ratio. At a 1:2 molar equivalence ratio, the T_g was decreased due to repulsion between free anions. At a 1:1 molar equivalence ratio, ion pairs started to form. Less free metal ions were, therefore, able to form transient crosslinks, which weakened the polymer-salt interaction and lead to microphase separation between the polymer and the salt, and, consequently, reduced physical properties (7).
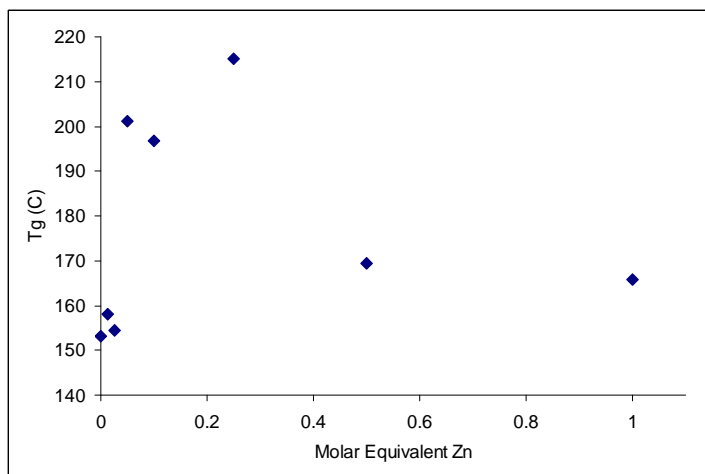

Figure 1. The glass transition temperatures as determined by DSC of P4VP/Zn complexes at various molar equivalent loadings of $ZnCl_2$.

We also examined the addition of HCl and other salts, including $CuCl_2$, $MgCl_2$, NaCl, and KCl, at 0.25 molar equivalents (see table 1). HCl was added as a proof of concept to demonstrate the effect of breaking up the hydrogen bonding of the pyridine nitrogens and forming electrostatic repulsions between chains. Sodium (Na^+) and Potassium (K^+) represent different ligation geometry compared to Zn^{2+} and copper (II) (Cu^{2+}), as they are monovalent rather than divalent species with larger ionic radius, and were investigated to determine whether they would have a similar effect as protonation—and, thus, electrostatic repulsion—on the thermal properties of P4VP. Magnesium (Mg^{2+}) is a divalent ion like Zn^{2+} and Cu^{2+}, but has a smaller ionic radius and was, therefore, expected to behave somewhere in between the purely coordination bonding of Zn^{2+} and Cu^{2+} 1 and the ionic interaction of the monovalent salts.

Table 1. Coordination geometry and T_g of metal salts coordinated with P4VP.

Metal Salt	T_g (ºC)	Coordination Geometry
No salt	147.13	N/A
ZnCl₂	215.03	Tetrahedral
CuCl₂	139.79	Square planar
NaCl	141.62	Ionic
KCl	146.62	Ionic
MgCl₂	ND*	Octahedral
CaCl₂	ND*	CR 3-9**

*T_g not detected, **Coordination numbers 3-9 possible

Coordination of P4VP with Cu^{2+} improved the T_g about 20 °C compared to the 70 °C enhancement with the same 0.25 molar equivalent loading of Zn^{2+}. Higher loadings of Cu^{2+} suppressed the T_g below neat P4VP levels. As discussed previously, Cu^{2+} and Zn^{2+} are both divalent, and are of similar ionic and atomic radii, but they differ by 1 d electron in their valence shells. Zn^{2+} has a full d shell (10 electrons) and preferentially forms tetrahedral coordination with ligands, whereas Cu^{2+} with 9 d electrons prefers a distorted tetrahedral or square planar geometry. Since the square planar geometry is less compact than tetrahedral, greater increases in interchain distance between crosslinks could result in less chain rigidity and a lower T_g.

As we expected, the T_g was suppressed by the addition of the acid (110 °C), as the electrostatic repulsion of the protonated P4VP increased interchain distances. The T_g of the NaCl and KCl/P4VP complexes also suppressed the T_g but to a much lesser extent—141 °C and 146 °C, respectively—compared to neat P4VP (147 °C). The minimal impact of the former salts can be explained by the TGA data, which showed virtually no ash remaining, indicating that essentially no salt was present in the solid P4VP/salt complex. Mg^{2+}, on the other hand, had a large effect on the thermal properties of the system. Although the T_g of the 0.25 molar equivalent system was not able to be determined, the thermal stability of the polymer was improved slightly, as evidenced by an increase in the decomposition temperature from 400 °C to 417 °C. In addition, the 23% ash remaining suggested a high degree of complexation. Since this study focused on Zn^{2+} coordination, further studies into the Mg/P4VP coordination may be warranted.

In order to gain further insight into the thermal changes in the P4VP system, as well as the degree of crosslinking, the thermal stability was probed with TGA. Figure 2 displays a typical TGA and DTGA spectra for native P4VP, with the weight percent shown on the left for the curve and the derivative weight on the right for the peaks. The maximum weight loss occurred at 400 °C, corresponding to degradation of the polymer backbone, and a small peak occurred at around 150 °C due to loss of moisture. Figure 3 shows the TGA spectra of P4VP with the addition of 0.11 molar equivalents of Zn^{2+}. In this case, the maximum weight loss due to the decomposition of the backbone occurred at a slightly lower temperature (376 °C), as has been observed for other polyelectrolytes (9). A second peak of approximately 550 °C was due to the decomposition of the ZnCl₂, although the salt did not burn entirely, as the final weight loss was only 85%. Figure 4 displays the remaining ash determined from TGA spectrums of various

molar equivalents of Zn^{2+} from 0.01 up to 1. The ash content increased from 0.01 up to 0.25 molar equivalent Zn^{2+}, and then decreased with higher loadings, following the same trend as the T_g data (figure 1). This suggests that the single Zn^{2+} per four pyridine nitrogens, or tetrahedral coordination of Zn^{2+}, is optimal in terms of thermal properties (see figure 5). In figure 6, the weight percent remaining is plotted as a function of weight percent $ZnCl_2$ added. Again, the same parabolic relationship is observed, but in this case a direct comparison between the amount of Zn^{2+} added and the amount actually incorporated in the polymer can be made. For loadings of Zn^{2+} up to approximately 25 wt %, the amount added matches the weight percent remaining. For loading levels higher than 25 wt %, the weight percent remaining is greatly reduced, indicating that the excess salt was not incorporated into the polymer system. It is interesting to note that the addition of more than 25 wt % results in 10–15 wt % remaining instead of the optimal 25 wt %. As a consequence, the thermal properties of the system are reduced by adding excess zinc salt, despite the fact that this salt is not incorporated, which could be due to the formation of salt ion pairs as already discussed. The excess salt could induce destabilization of the polymer chains during the complex formation process, as crosslinks are initially formed with all or most of the zinc ions, and are later broken in the washing and drying steps. A visual inspection of the polymers formed with different amounts of Zn^{2+} appears to suggest quite different densities of the materials, depending on the amount of Zn^{2+}—with the higher loadings having lower densities.
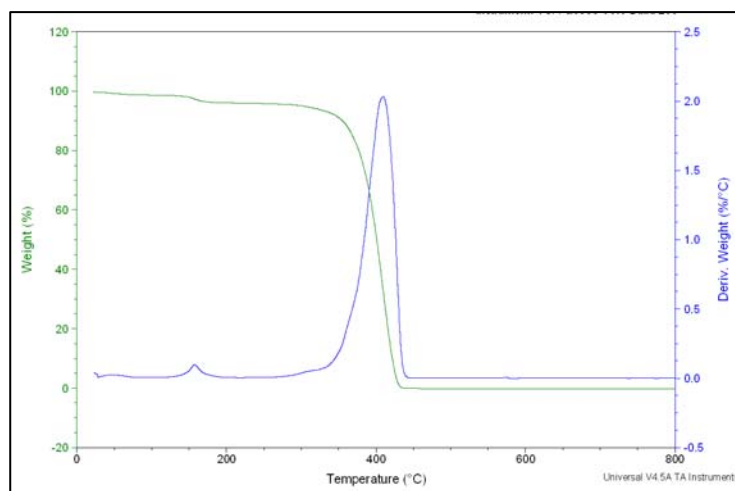

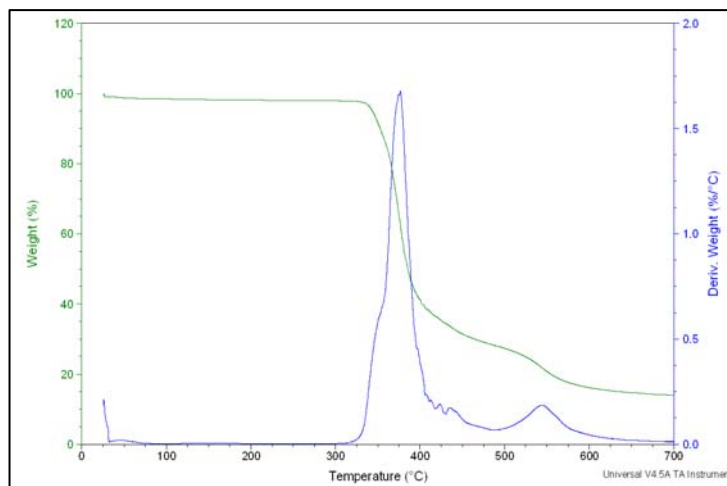Figure 2. TGA (left) and DTGA (right) spectrum of P4VP.

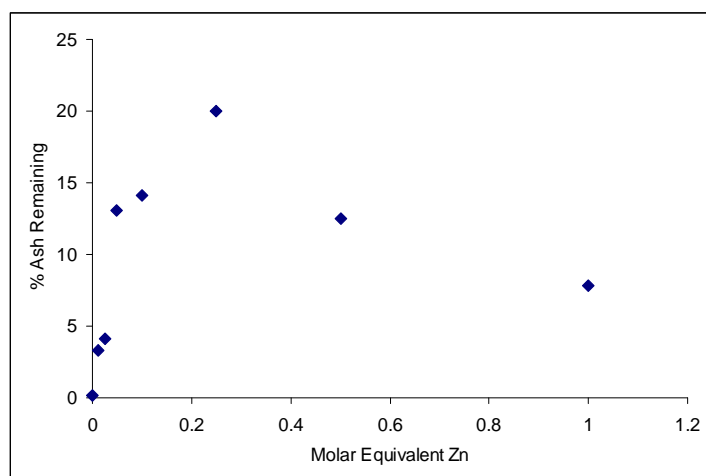Figure 3. DTGA spectrum of P4VP with 0.11 molar equivalents Zn.

Figure 4. Remaining ash of the P4VP/Zn complex as a function of
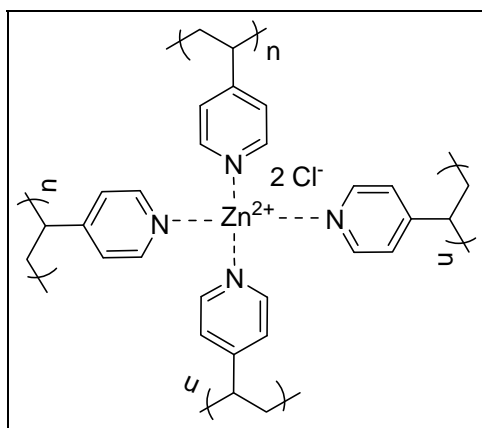Zn loading as determined by TGA.

Figure 5. Possible tetrahedral coordination
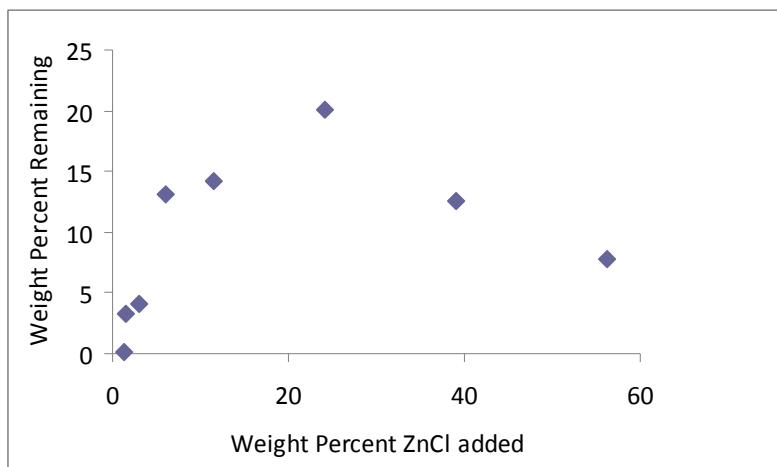complexation of $ZnCl_2$ with P4VP.

Figure 6. Weight percent ZnCl$_2$ added versus total weight percent remaining
as determined by TGA.

As evidenced by the aforementioned results, the addition of metal salts alters the thermal properties and stability of the polymer system. The thermal properties can be tailored based on the type and amount of salt added. In order to better understand how the amount added equates with the degree of crosslinking, or the actual fraction of the pyridine rings in the polymer that are coordinated, the polymer complexes were analyzed with FTIR. Figure 7 displays peaks of characteristic pyridine ring vibrations at 1595 cm^{-1} for free uncoordinated rings and at 1622 cm^{-1} for coordinated rings at various loadings of Zn^{2+}. As is shown, the peak height intensities follow the same trend as observed with the thermal data, in that the 1:4 molar ratio, or tetrahedral coordination of the Zn^{2+} with the pyridine rings, yields the highest fraction of the rings in the coordinated state, as evidenced by the highest relative peak intensity at 1622 cm^{-1}. Integrated peak areas were determined by CasaXPS software, and the area fractions of the coordinated peaks at characteristic pyridine ring vibrations (1622 cm^{-1}), and pyridine C-H in and out of plane bending (1031 cm^{-1}), are shown in figure 8. The trend is parabolic with 0.25 molar equivalents of Zn^{2+} at the maximum as expected but with one variation—0.5 molar equivalents of Zn^{2+} is also at the maximum. It appears that 60% of the pyridine rings or P4VP repeat units are the most that can be crosslinked or coordinated due to electrostatic repulsion and chain entanglements, and, thus, this level is reached with both loadings of zinc salt. This suggests that the same fraction of rings are coordinated in both cases but with obvious different thermal property effects. In the former case, the amount of salt added is optimal, hence all of the added salt forms coordination crosslinks with the polymer backbone. In the latter case, only a portion of the salt added forms crosslinks, and the excess salt has a potentially destabilizing effect on the system, as discussed previously. Maximum coordination is not achieved for loadings of Zn^{2+} beyond 0.5 molar equivalents for reasons discussed previously.

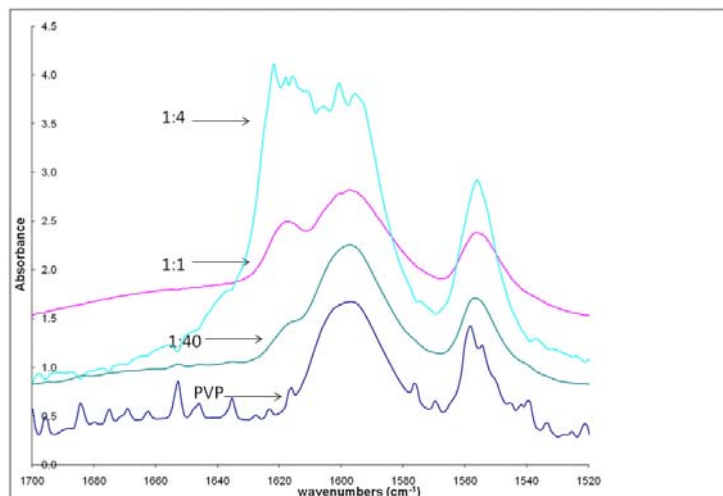Figure 7. FTIR spectra of P4VP recorded at varying molar equivalent
ratios of Zn^{2+} : P4VP. The peak on the right corresponds to the
uncoordinated pyridine rings whereas the peak on the left at
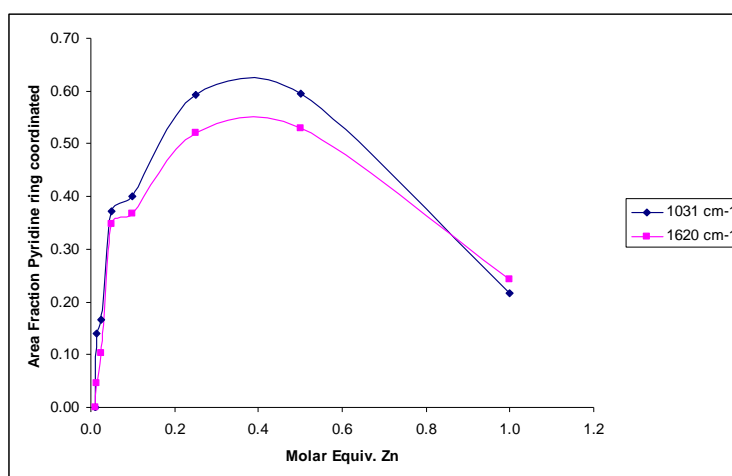1620 cm^{-1} represents the fraction of the coordinated pyridine
rings in the polymer.

Figure 8. Area fraction of coordinated pyridine rings versus molar
equivalent Zn^{2+} added as determined by FTIR spectrums.

4. Conclusions

The addition of metal salts to poly (4-vinyl pyridine) alters the thermal properties of the polymer, with the extent of alteration being highly dependent on the type and loading of the salt. Negligible changes in T_g were observed for ionic-based ligation, while substantial T_g enhancements were seen for coordination-based ligation. The greatest T_g enhancement of the P4VP system (70 °C) was observed with the addition of Zn^{2+} at a 0.25 molar equivalent loading. The former loading was determined to be the optimal one based on T_g, as well as ash content from TGA and a fraction of coordinated pyridine rings from FTIR data. Further characterization of these systems in order to determine material density and conductivity is of interest. In addition, a more thorough study of other salts, including Mg^{2+}, could yield even greater enhancement of the P4VP's thermal properties.

5. References

1. Atornigitjawat, P.; Runt, J. Ion Conduction and Polymer Dynamics of Poly(2-vinylpyridine)-lithium Perchlorate. *Journal of Physical Chemistry* **2007**, *111*, 13483–13490.

2. Rodrigues, J.; Goncalves, J.; Mangrich, A.; Soldi, V.; Bertolino, J.; Pires, A. Thermal Behavior and Electrical Conductivity of Poly(vinyl pyridine)/Copper Complexes. *Advances in Polymer Technology* **2000***, 19*, 113–119.

3. Kuo, S.; Wu, C.; Chang, F. Thermal Properties, Interactions, Morphologies, and Conductivity Behavior in Blends of Poly(vinylpyridine)s and Zinc Perchlorate. *Macromolecules* **2004***, 37, 192–200.

4. Belfiore, L.; Graham, H.; Ueda, E. Ligand Field Stabilization in Nickel Complexes that Exhibit Extraordinary Glass Transition Temperature Enhancement. *Macromolecules* **1992**, *25*, 2935–2939.

5. Rafique, U.; Mazhar, M.; Ali, S.; Khwaja, F. Analytical and electrical studies on poly(2-vinylpyridine) and its metal complexes. *Synthetic Metals* **1996**, *78*, 73–77.

6. Belfiore, L.; Pires, A.; Wang, Y.; Graham, H.; Ueda, E. Transition-metal Coordination in Polymer Blends and Model Systems. *Macromolecules* **1992**, *25*, 1411–1419.

7. Kim, J.; Min, B.; Won, J.; Kang, Y. Analysis of the Glass Transition Behavior of Polymer-salt Complexes: An Extended Configurational Entropy Model. *Journal of Physical Chemistry* **2003**, *107*, 5901–5905.

8. Fairley, N.; Carrick, A. *The Casa Cookbook Part 1: Recipes for XPS Data Processing*; Acolyte Science: Chesire, UK, 2005.

9. Suleiman, D.; Napadensky, E.; Sloan, J.; Crawford, D. Thermogravimetric Characterization of Highly Sulfonated Poly(styrene-isbutylene-styrene) Block Copolymers: Effects of Sulfonation and Counter-ion Substitution. *Thermochimica Acta* **2007**, *460*, 35–40.

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